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(54) Title: PROCESS FOR PREPARING CELLULOSE ESTERS USING A SULFONIC ACID RESIN CATALYST			
(57) Abstract <p>The present invention relates to a process for preparing cellulose esters having a total DS/AGU of 0.1 to 3.0, said process consisting of contacting the following: (i) a cellulose material, (ii) a solubilizing amount of a solvent system comprising a carboxamide diluent or a urea-based diluent, (iii) an acylating reagent, and (iv) an insoluble sulfonic acid resin catalyst.</p>			

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PROCESS FOR PREPARING CELLULOSE ESTERS
USING A SULFONIC ACID RESIN CATALYST

Field of the Invention

5 This invention relates to a process for the preparation of esters of cellulose having a DS/AGU of between 0.1 and 3.0 where the cellulose or cellulose derivative is contacted with an acylating reagent, an insoluble sulfonic acid resin catalyst, and a
10 carboxamide diluent or a urea-based diluent.

Background of the Invention

15 Cellulose esters (CEs) are conventionally synthesized by the reaction of cellulose with the anhydride or anhydrides corresponding to the desired ester group or groups, using the corresponding carboxylic acid as diluent and product solvent.

20 In these processes, the reaction mixture is heterogeneous initially due to the insolubility of cellulose in most organic solvents including carboxylic acids. The reaction is terminated when the cellulose derivative has gone into solution and the desired solution viscosity has been reached. When the mixture becomes homogeneous, the cellulose is fully or almost
25 fully acylated.

30 Optionally, one may use a large excess of sulfuric acid catalyst, in which case the product is a cellulose alkanoate sulfate. Selective cleavage of the sulfate groups can afford a partially substituted cellulose alkanoate. It is, however, extremely difficult to remove a large DS (degree of substitution) of sulfate esters without simultaneously reducing the DP (degree of polymerization) of the cellulose ester to unacceptable levels.

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Thus, in conventional processes, the synthesis of partially substituted cellulose esters is accomplished by hydrolysis of cellulose triesters, prepared by mineral acid catalyzed acylation in a separate step, to 5 the desired level of substitution. Typically, hydrolysis in a mixture of water and carboxylic acid solvent results in scrambling of position of substitution (due to acyl migration and simultaneous, but slower, reesterification of the newly exposed 10 hydroxyl groups by the carboxylic acid solvent) so that the products have an equilibrium distribution of ester substituents.

Partially substituted cellulose esters have great commercial value. They are used in coatings, where 15 their greater solubility (in comparison with triesters) and hydroxyl group content (to facilitate crosslinking) are prized. In plastics, fibers, and film applications, the ability to synthesize partially substituted CEs permits control over thermal, mechanical, 20 biodegradation, and compatibility properties.

It is well known in the art that esters of cellulose with long-chain carboxylic acids could be prepared by acylation with the corresponding acid chlorides in pyridine or, less successfully, other 25 solvents. This method was useful only for synthesis of cellulose triesters. For example, see Malm, et al., Ind. Eng. Chem., 1951, 43, 684-688.

United States Patent 2,705,710 discloses DMAc as a solvent and sulfuric acid as a catalyst to make 30 cellulose triacetate (a fully substituted ester - 2.9 DS Ac and 0.10 DS sulfate). The reaction disclosed in this patent is run at 140°C and, therefore, is very fast. The disadvantage of the sulfuric acid technology of United States Patent 2,705,710 is the need for a

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hydrolysis step in order to obtain partially substituted cellulose esters.

Direct synthesis of partially substituted CEs has also been taught previously by acylation of cellulose in solution as shown in United States Patent 2,976,277. If cellulose is first dissolved in a mixture of lithium chloride and an amide solvent (either 1-methyl-2-pyrrolidinone (NMP) or N,N-dimethylacetamide (DMAC)), it can then be acylated with a carboxylic anhydride in the presence or absence of a catalyst to afford a partially or fully substituted CE depending only on the equivalents of anhydride added. Esters of cellulose with long-chain carboxylic acids have been made in this way. Thus, in Carbohydrate Polymers, 22, 1-7, 1993, it is disclosed that it is possible to react cellulose in DMAC/LiCl solution with a variety of carboxylic acid chlorides using amine catalysis, or alternatively carboxylic acids using dicyclohexylcarbodiimide catalysis, to obtain esters of cellulose with acids of chain length up to 18 carbons (stearate) and DS 0.1 to 2.5. While this method has great flexibility in terms of the nature of the anhydride and the DS of the product obtained, the necessity for dissolving cellulose means that reaction mixtures must be dilute (no more than 5% cellulose) and that the process is lengthened by the time it takes for cellulose dissolution. It is a practical necessity to develop a method to recycle the expensive lithium chloride with high efficiency, which method has not yet been disclosed.

Long-chain (carbon chain length greater than 4) esters of cellulose (LCCEs) are known from the pioneering work of Malm as shown in Ind. Eng. Chem., 43, 684-691, 1951. Efforts to obtain LCCEs by reaction of cellulose with long-chain anhydrides in carboxylic acid solvent with mineral acid catalysis have not been

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successful because the esterification rate is too slow and cannot compete with the rate of chain cleavage.

The only other methods known in the literature involve the use of "impeller" reagents such as 5 chloroacetic anhydride, as disclosed in United States Patent 1,880,808, and the reaction of regenerated cellulose with long-chain acid chlorides in pyridine or, as disclosed in Ind. Eng. Chem. Res., 31, 2647-2651, 1991, neat. The impeller reagents tend to be expensive, 10 toxic, and difficult to handle.

Regenerated cellulose is expensive, as are acid chlorides, which also require reactors of corrosion-resistant construction. Additionally, direct reaction of cellulose with acid chlorides under vacuum does not 15 result in homogeneous, soluble products.

LCCEs are of interest commercially because of their lower processing temperatures, greater impact strength, greater solubility in less polar solvents, the likelihood of greater compatibility with hydrophobic 20 polymers, the potential for formation into molded or extruded objects without the need for a plasticizer, and their potential utility as associative thickeners for water-based paints (by analogy with long-chain ethers of cellulose, such as hydrophobically-modified 25 hydroxyethylcellulose).

It has been also disclosed in United States Patent 2,705,710 that activation of cellulose with N,N-dialkylamides prior to conventional (mineral acid and carboxylic anhydride) esterification permits rapid 30 esterification without excessive degradation. The patent also discloses that this is a process for making cellulose triacetate with inherent viscosity in the range of 1.1 to 1.3 (less than that required for many current commercial applications).

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In United States Patent 2,861,069, it is disclosed that sulfonated polystyrene resins are effective catalysts for acylation of cellulose by carboxylic anhydrides in the corresponding carboxylic acid solvent.

5 Disadvantages of the method include: (1) that a large excess of anhydride is required to prevent undesirable chain degradation, and (2) that only fully substituted esters may be prepared in this way unless a separate hydrolysis step is included.

10 Clearly, a need exists in the art for a process by which CEs of less than full substitution can be prepared directly from cellulose. The process must be economical, practical, and amenable to industrial production. It should be possible with this process to 15 synthesize products which have sufficiently high molecular weight for their particular commercial application. It would be desirable to be able to use long-chain anhydrides in this process, such that cellulose esters containing long-chain ester groups 20 could be obtained. It is essential that the products be sufficiently homogeneous so that they can be processed thermally and/or in solution, to be useful for film, coatings, plastics, and certain other applications. It is desirable to use a catalyst which could be physically 25 separated from the product by simple techniques such as filtration and which could, therefore, easily be recovered for re-use. It is also desirable to have the ability to control product DS and molecular weight by practical and predictable adjustments to process 30 conditions.

Summary of the Invention

This invention relates to preparation of cellulose esters (CEs) of degree of substitution (DS) less than 35 3.0 by reaction of cellulose in a carboxamide diluent or

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a urea-based diluent (optionally containing an additional cosolvent), with a acylating reagent such as carboxylic acid anhydride, using an insoluble sulfonic acid resin catalyst.

5 More particularly, this invention relates to a process for preparing cellulose esters having a total DS/AGU of 0.1 to 3.0, said process comprising of contacting the following:

10 (i) a cellulose material,
(ii) a solubilizing amount of a solvent system comprising either a carboxamide diluent or a urea-based diluent,

15 wherein the carboxamide portion of said carboxamide diluent comprises the structure: R⁴R⁵NCOCR⁶R⁷R⁸, wherein R⁴, R⁵, R⁶, R⁷, and R⁸ are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms, and

20 25 wherein said urea portion of said urea-based diluent comprises the structure: R⁹R¹⁰NCONR¹¹R¹², wherein R⁹, R¹⁰, R¹¹, and R¹² are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms,

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(iii) an acylating reagent selected from the group consisting of

(a) an acid chloride, and optionally, an acid acceptor,

5 (b) a carboxylic acid anhydride,

(c) diketene, ketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, and an ester of acetoacetic acid,

(d) an ester of a carboxylic acid,

10 and combinations of one or more of (a)-(d), and

(iv) an insoluble sulfonic acid resin catalyst; wherein said components (i) and (ii) are contacted first and components (iii) and (iv) are contacted with the product of said contacting of components (i) and (ii), in any order.

20 Preferably, the invention relates to a process for making esters of cellulose with long-chain carboxylic acids (containing more than 4 carbon atoms).

25 The advantages of this process over the prior art include: being able to use cellulose with a lower alpha content and a lower molecular weight, synthesis of partially or fully substituted esters of cellulose with long-chain carboxylic acids and, optionally, short-chain acids, and the ability to obtain partially substituted cellulose esters. These partially substituted cellulose esters have good solubility in a wide range of organic solvents and can have high molecular weight. For the 30 purposes of this invention, long-chain shall refer to greater than 4 carbons, while short-chain shall refer to 4 carbons or less.

35 The process of the invention has broad utility for the economical, direct synthesis of cellulose esters for plastics, film, fiber, and coatings applications.

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Detailed Description of the Invention

As used herein, the term "degree of substitution" or "DS" or "DS/AGU" refers to the average number of acyl substituents per anyhydroglucosidic ring of the cellulose polymer.

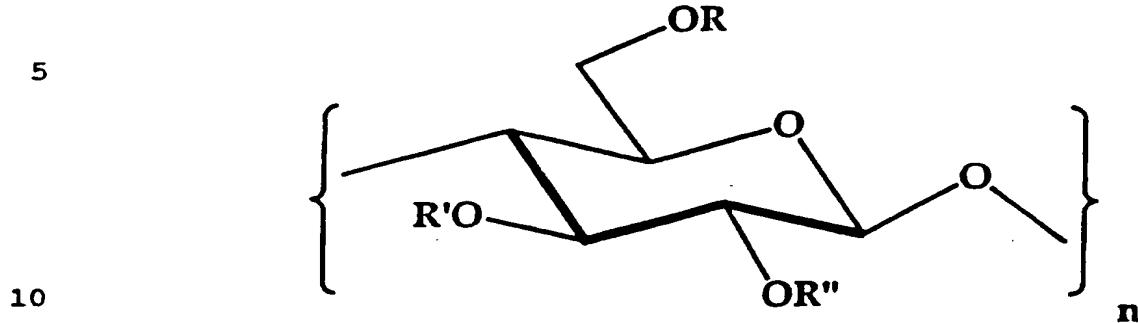
The present invention relates to a process for preparing a cellulose ester having a total DS/AGU of 0.1 to 3.0, preferably 2.0 to 3.0, more preferably 2.4 to 2.9, said process consisting of contacting the following:

- (i) a cellulose material,
- (ii) a solubilizing amount of a solvent system comprising either a carboxamide diluent or a urea-based diluent,
- (iii) an acylating reagent selected from the group consisting of
 - (a) an acid chloride, and optionally, an acid acceptor,
 - (b) a carboxylic acid anhydride,
 - (c) diketene, ketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, and an ester of acetoacetic acid,
 - (d) an ester of a carboxylic acid, and combinations one or more of (a)-(d),
- and
- (iv) an insoluble sulfonic acid resin catalyst.

Components (i) and (ii) are usually contacted first and components (iii) and (iv) are contacted with the product of said contacting of components (i) and (ii), in any order.

The cellulose esters produced by the invention generally comprise the following structure:

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wherein R, R', and R'' are selected separately from the group consisting of: hydrogen, with the proviso that R, R', and R'' are not all hydrogen simultaneously; acetoacetyl; and $R^1C=O$ 20 wherein R^1 is alkyl having from about 1 to about 30 carbons; carboxyalkyl of the structure $(CH_2)_nCO_2H$, where n is from 2 to 6, preferably from 2 to 4; carboxyalkenyl of the structure, $CR^2=CR^3CO_2H$, where R^2 and R^3 are independently selected from the group consisting of hydrogen, methyl, branched alkyl having from about 1 to about 30 carbons, phenyl, and naphthyl; alkenyl having from about 1 to about 30 carbon atoms and from one to three double bonds; and branched 25 alkenyl having from about 1 to about 30 carbon atoms and having from one to three double bonds. 30 For carboxyalkenyl, alkenyl and branched alkenyl, the double bonds present may be in the cis or trans position.

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It is preferred that R, R' and R'' are independently selected from the group consisting of hydrogen, acetyl, propionyl and butyryl for the cellulose ester structure indicated above. The long-chain esters are also preferred.

The carboxamide portion of the carboxamide diluent comprises the structure: $R^4R^5NCOCR^6R^7R^8$, wherein R⁴, R⁵, R⁶, R⁷, and R⁸ are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, substituted phenyl, phenyl, substituted naphthyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms.

Examples of the carboxamide diluents are 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylpropionamide, N,N-diethylacetamide, or N,N-dimethylacetamide (DMAC). DMAC is particularly preferred.

Carboxamides such as succinimides, phthalimides or glutarimides may also be used as diluents.

The urea portion of the urea-based diluent comprises the structure: $R^9R^{10}NCONR^{11}R^{12}$, wherein R⁹, R¹⁰, R¹¹, and R¹² are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms.

Urea compounds useful in the diluents of this invention also intended within the scope of the general definition are ones wherein one of R⁹ and R¹⁰ and one of R¹¹ and R¹² are connected to form a cyclic urea, such as N,N-dimethylimidazolidinone. Preferred urea compounds are ones selected from the group consisting of urea and

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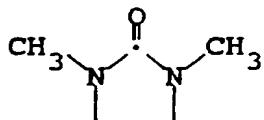
N,N-dimethylimidazolidinone. N,N-dimethylimidazolidinone has the structure:

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Amino acids such as proline or glycine may also be used as diluents.

The ratios of solvent to cellulose used can vary within a moderately wide range.

25 For the purposes of this invention, examples of alkyl having from about 1 to about 20 carbon atoms are methyl, ethyl, propyl, butyl, hexyl, nonyl, hexadecyl, and alkyl including aryl substituted alkyl such as benzyl, cycloalkyl such as cyclohexyl, etc. Examples of 30 branched alkyl having from about 1 to about 20 carbon atoms are isopropyl, isobutyl, isononyl, tertiary butyl, etc. Examples of alkenyl are propenyl, decenyl, pentadecenyl, (Z)-heptadec-8-enyl, and (Z,Z)-heptadecadi-8,11-enyl. Examples of branched alkenyl are 35 pentadecenyl.

Other activated acyl derivatives such as acid chlorides, are also useful; in the case of acid chlorides an acid acceptor such as pyridine, sodium bicarbonate, or sodium acetate may optionally be used as 40 well. The acylating reagents may also include diketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one (TKD), or an ester of acetoacetic acid. As taught by Witzeman in Tetrahedron Letters, 1990, 31, 1401-1404, tert-butyl acetoacetate (tBAA) is an especially suitable aceto-

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acetate ester because it generates the reactive intermediate, acetylketene, at a high rate.

Preferred acid chlorides are acetyl chloride, propionyl chloride, butyryl chloride, hexanoyl chloride, 5 lauroyl chloride, palmitoyl chloride, and stearoyl chloride. In the case of acid chlorides, an acid acceptor such as pyridine, sodium bicarbonate, or sodium acetate may optionally be used in combination with the acylating reagent.

10 Preferred in this invention are carboxylic anhydrides selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, hexanoic anhydride, nonanoic anhydride, lauric anhydride, palmitic anhydride, and stearic anhydride.

15 Preferred acylating reagents in this invention are esters of carboxylic acids which are selected from the group consisting of the following acids: capric, lauric, palmitic, stearic, oleic, linoleic, linolenic, cyclohexanedicarboxylic, benzoic, substituted benzoic, 20 phthalic, isophthalic and terephthalic.

25 Acid acceptors useful within the context of this invention are selected from the group consisting of pyridine, triethylamine, sodium bicarbonate and sodium acetate. The term "acid acceptor" is generally meant refer to a basic material, such as a Lewis base. Pyridine is a preferred acid acceptor.

Preferred cellulose esters made by the process of this invention include cellulose acetate, cellulose butyrate, cellulose propionate, cellulose acetate 30 butyrate, cellulose acetate propionate, cellulose acetate hexanoate, cellulose acetate nonanoate, cellulose acetate laurate, cellulose palmitate, cellulose acetate stearate, cellulose nonanoate, cellulose hexanoate, cellulose hexanoate propionate, and 35 cellulose nonanoate propionate.

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A wide variety of sources of cellulose may be used for the practice of this invention. Cellulose sources useful in our invention include hardwoods, softwoods, cotton linters, bacterial cellulose, and regenerated 5 cellulose.

The practice of the current invention allows for a wide variety of cellulose starting materials, temperatures, concentrations, insoluble sulfonic acid resin catalysts, carboxylic acid anhydrides, 10 nonsolvents, and reactant ratios. A wide variety of cellulose esters may be produced, depending on the conditions selected.

15 Temperatures employed for all aspects of the process of the invention are in the range of about 0°C to about 200°C, preferably about 100°C to about 180°C, and more preferably, about 120°C to about 170°C.

20 The insoluble sulfonic acid resin catalysts are easily separated from the reaction mixture by methods known in the art, such as filtration and can therefore be repeatedly re-used.

25 The products are isolated by methods known in the art, for example by adding a nonsolvent (often water) to the reaction mixture after separation of the catalyst, and isolating the precipitated product by filtration and washing.

In this invention, a combination of carboxamide or urea with an insoluble sulfonic acid resin catalyst is employed wherein the carboxamide or urea functions as an activating agent, diluent, and a solvent.

30 In the process of the invention, the molar ratio of component (iii):component (iv) is that amount that will result in the desired DS/AGU under the chosen reaction conditions. Conditions suitable for the formation of cellulose esters can vary widely. The 35 cellulose must first be activated by contacting with the

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amide-based diluent or urea-based diluent. This may be most simply accomplished by heating a slurry of the cellulose in the amide-based diluent or urea-based diluent to a temperature of 100-180°C, although it is 5 also possible to accomplish the activation by prolonged contact at room temperature.

The acylating reagent(s) is typically added all at once. The total amounts of acylating reagents used can vary from 3 to 10 equivalents based on equivalents of 10 anhydroglucose units, with 4 to 6 equivalents most preferred. Within this total the proportion of each acylating reagent may be varied to achieve the desired DS of each substituent in the product.

It is preferable that the amount of cellulose 15 material present is about 1.0 percent to about 50 percent, preferably about 9.0 percent to about 28 percent, based on the weight of said carboxamide-based diluent or urea-based diluent, and the amount of said 20 insoluble sulfonic acid resin catalyst is about 0.1 percent to about 100 percent, preferably about 5.0 percent to about 50 percent, based on the weight of said cellulose material.

The process of this invention usually includes the additional step of insolubilizing the cellulose ester by 25 addition of an insolubilizing amount of a nonsolvent. It may also include the step of separating the insolubilized cellulose ester.

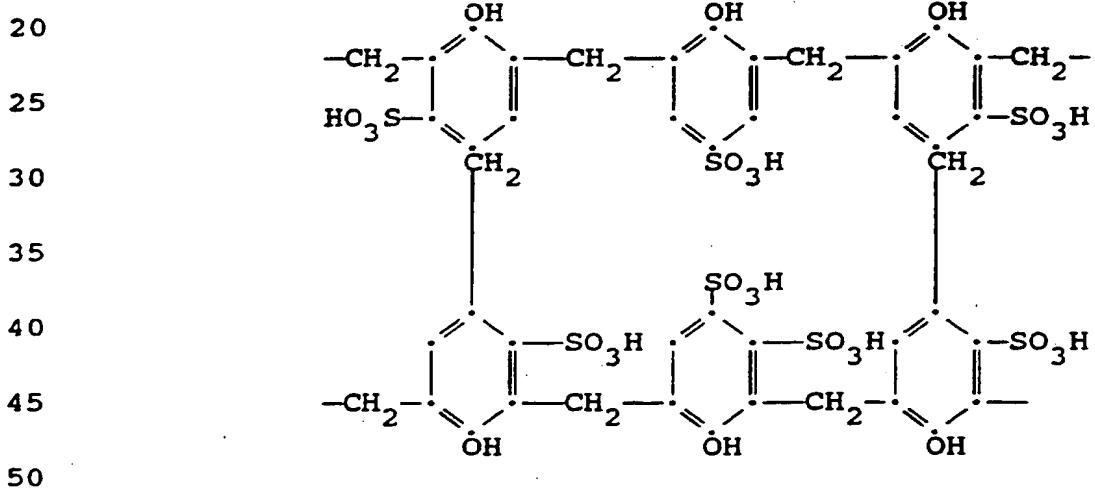
Nonsolvents referred as being useful for the 30 isolation of cellulose esters manufactured by this process will be specific to the particular material. They should dissolve the reaction solvents and any by-products, but should be nonsolvents for the cellulose ester. Examples include methanol, ethanol, 2-propanol, and water.

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The insoluble polymeric type sulfonic acids which are preferred as catalysts in the manufacture of the esters of cellulose of the invention are those which are ordinarily known as sulfonic acid type ion exchange 5 resins. They contain the active sulfonic acid radicals chemically bound to a cross linked polymeric structure. Normally they are of one of the following two types:

I. Polyvinyl aryl compounds and monovinyl aryl compounds such as sulfonated copolymers of styrene and 10 divinyl benzene, for example, Amberlyst XN-1010 commercially available from Rohm & Haas and Dowex 50-X20-200 commercially available from Dow Chemical Company.

II. Sulfonated condensation polymers of phenol and 15 formaldehyde.



Sulfonic acid type ion exchange resins can be described as high molecular weight poly acids which are 55 insoluble in aqueous and nonaqueous media. They comprise an insoluble cross-linked back-bone polymer structure to which are fixed sulfonic acid groups which present hydrogen ions. The number of sulfonic acid groups present in the ion exchange resin determine its

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effectiveness as a catalyst along with the size of the insoluble resin. Although these two factors can vary over a relatively wide range and the resin will still exhibit catalytic properties the more are those

5 described in U.S. Patent No. 2,366,007 of D'Alelio and the sulfonic acid ion exchange resins described in chapter 5 of the book entitled "Ion Exchange Resins" by Kunin and Meyers (John Wiley and Sons, 1950).

10 The products of the process of this invention are useful for various purposes such as for plastics, film, fiber, and coatings applications.

DS or DS/AGU can be determined for the cellulose esters of this invention by any method known in the art, for example, by proton NMR.

15 This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless 20 otherwise specifically indicated. The starting materials are commercially available unless otherwise described. All percentages are by weight unless otherwise described.

25

EXAMPLES

In the following examples, the cellulose and carboxamide or urea-based solvent were added to a three-neck round bottom flask equipped with mechanical stirrer, thermometer, nitrogen inlet, and distillation head. The slurry was heated to 100°C under nitrogen, with stirring. Then the anhydride(s) and the catalyst (Amberlyst XN-1010, 1 part by weight per 4 parts by weight cellulose) were added to the activated cellulose, and the mixture was heated to reaction temperature.

35 Note that "equiv" below refers to equivalents of reagent

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per anhydroglucose unit of cellulose. In each example, the mixture was stirred at the reaction temperature until it was clear and smooth, except for the presence of the polymeric catalyst. The solution then was cooled 5 to 20-80°C. The catalyst was removed by filtration (sometimes the reaction mixture was diluted with acetone or the amide or urea diluent first to reduce viscosity). The product was precipitated by adding the filtrate dropwise to water or methanol in water with strong 10 agitation. The product was isolated by filtration, then was slurried again in water or in methanol in water. This process was repeated two to five times as required to remove all impurities from the product. The product was dried in a vacuum oven under nitrogen at 40-80°C. 15 The yields quoted in the examples are of isolated, well-characterized products. DS was determined by ^1H NMR in d-6 DMSO containing several drops of trifluoroacetic acid (to shift any hydroxyl protons downfield), or by hydrolysis of a sample of the 20 cellulose ester followed by quantification of liberated carboxylic acids by gas chromatography. Gel permeation chromatography used NMP as solvent (polystyrene reference). Intrinsic viscosity was measured in phenol/tetrachloroethane (60/40) solution. Differential 25 scanning calorimetry (20°C/min, second scan, maximum temperature 240°C) was employed to determine T_g 's. Sulfur content was measured by X-ray fluorescence. Representative members of each family of materials were examined by infrared spectroscopy to confirm product 30 identity. All temperatures in degrees centigrade.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not 35 intended to limit the scope of the invention unless

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otherwise specifically indicated. The starting materials are commercially available unless otherwise indicated.

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EXAMPLE 1

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX-hardwood pulp, available from International Paper in Natchez, Mississippi
15	Carboxylic Anhydride Equiv	Acetic anhydride 6
	Reaction Temperature	120 °C
20	Amide Diluent	DMAC
	g Amide/g Cellulose	10
	Reaction Time	5.3 hours
25	Key Analyses	DS(acetyl) = 2.88, IV = 2.48, GPC M_n = 125,000, soluble in DMSO and NMP, sulfur content = 224 ppm.

30 This example demonstrates direct synthesis from cellulose of a partially substituted, high molecular weight cellulose acetate with good solubility in organic solvents.

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EXAMPLE 2

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride Equiv	Propionic anhydride 6
20	Reaction Temperature	150 °C
25	Amide Diluent	DMAC
	g Amide/g Cellulose	10
	Reaction Time	1.6 hours
	Key Analyses	DS(propionyl) = 2.58, IV = 1.42, GPC M_p = 52,300, T_g = 101 °C, soluble in DMSO and NMP, sulfur content = 285 ppm.

This example demonstrates synthesis of an amorphous, relatively high molecular weight, partially substituted 30 cellulose propionate with good solubility in organic solvents, directly from cellulose.

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EXAMPLE 3

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

	Cellulose	Natchez HVX
10	Carboxylic Anhydride Equiv	Propionic anhydride 4.22
15	Reaction Temperature	135 °C
20	Amide Diluent	DMAC
25	g Amide/g Cellulose	5
	Reaction Time	4.4 hours
	Key Analyses	DS(propionyl) = 2.67, IV = 0.82, GPC M_w = 36,500, T_g = 127 °C, T_m = 233 °C, soluble in DMSO and NMP.

This example demonstrates control over molecular weight by manipulating the amount of anhydride, the potential for using only slight excess of anhydride, the 30 capability to synthesize partially crystalline cellulose propionate, and that smaller amounts of amide diluent may be used.

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EXAMPLE 4

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride Equiv	Acetic anhydride 3.97
20	Carboxylic Acid grams per gram cellulose	Acetic Acid 15.7
25	Reaction Temperature	118 °C
30	Amide Diluent	None
35	g Amide/g Cellulose	0
	Reaction Time	0.5 hours
	Key Analyses	DS(acetyl) = 3.02, IV = 0.26, GPC M_n = 18,000, soluble in DMSO and NMP, sulfur content = 117 ppm.

This example demonstrates that in the absence of amide diluent a cellulose acetate product of low molecular weight and full substitution is obtained, which has very limited solubility in organic solvents.

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EXAMPLE 5

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride Equiv	Propionic anhydride 4.22
20	Carboxylic Acid grams per gram cellulose	Propionic Acid 9.93
25	Reaction Temperature	100 °C
30	Amide Diluent g Amide/g Cellulose	None 0
	Reaction Time	3.1 hours
	Key Analyses	DS(propionyl) = 3.04, IV = 0.16, GPC M_n = 5,900, T_g = 76 °C, T_m = 206 °C, soluble in acetone, acetic acid, THF, DMSO and NMP.

This example demonstrates that in the absence of amide diluent a cellulose propionate product of low molecular weight and full substitution is obtained.

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EXAMPLE 6

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride Equiv	Propionic anhydride 6.00
20	Reaction Temperature	150 °C
25	Amide Diluent	NMP
	g Amide/g Cellulose	10.33
	Reaction Time	8.6 hours
	Key Analyses	DS(propionyl) = 3.09, IV = 0.80, GPC M_w = 43,500, T_g = 109 °C, T_m = 237 °C, soluble in acetone, acetic acid, THF, chloroform, DMSO and NMP.

This example demonstrates that with NMP diluent a crystalline, highly soluble cellulose propionate product of moderate molecular weight and full substitution is obtained.

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EXAMPLE 7

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride Equiv	Propionic anhydride 4.00
20	Acetoacetylation Reagent Equiv	Diketene 1.0
25	Reaction Temperature	120 °C
30	Amide Diluent g Amide/g Cellulose	DMAC 9.37
35	Reaction Time	11.9 hours
	Key Analyses	DS(propionyl) = 2.54, DS(acetoacetyl) = 0.79 (high total DS may be due to some enol propionate), IV = 1.22, GPC M_w = 44,400, T_g = 122 °C, soluble in THF, acetic acid, acetone, $CHCl_3$, DMSO and NMP.
	This example demonstrates that it is possible to synthesize a mixed ester containing acetoacetyl groups by using amide diluent.	

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EXAMPLE 8

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
	Carboxylic Anhydride 1 Equiv	Acetic anhydride 2.0
15	Carboxylic Anhydride 2 Equiv	Hexanoic anhydride 2.0
	Reaction Temperature	150 °C
20	Amide Diluent	DMAC
	g Amide/g Cellulose	9.37
	Reaction Time	2.6 hours
25	Key Analyses	DS(acetyl) = 1.70, DS(hexanoyl) = 0.80, IV = 1.18, GPC M_n = 45,100, soluble in acetone, acetic acid, THF, $CHCl_3$, DMSO and NMP, T_g = 91 °C, T_m = 196 °C.
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This example demonstrates direct synthesis from cellulose of a partially substituted, mixed cellulose ester, where one of the ester groups is a long-chain ester, with good solubility in organic solvents.

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EXAMPLE 9

Reagents set forth below were subjected to the standard procedure described above under the standard reaction conditions, except as described below. The 5 results, in terms of identity of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Cellulose	Natchez HVX
15	Carboxylic Anhydride 1 Equiv	Acetic anhydride 2.0
20	Carboxylic Anhydride 2 Equiv	Lauric anhydride 2.0
25	Reaction Temperature	160 °C
30	Amide Diluent g Amide/g Cellulose	DMAC 9.37
	Reaction Time	1.1 hours
35	Key Analyses	DS(acetyl) = 1.95, DS(lauroyl) = 0.61, IV = 1.03, GPC M_n = 39,900, soluble in acetone, THF, $CHCl_3$, and NMP, T_g = 104 °C, T_m = 215 °C.

This example demonstrates direct synthesis from cellulose of a partially substituted, mixed cellulose ester, where one of the ester groups is a long-chain ester, with good solubility in organic solvents.

The invention has been described in detail with particular reference to preferred embodiments thereof, 40 but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. Moreover, all patents, patent applications (published and unpublished, foreign or

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domestic), literature references or other publications noted above are incorporated herein by reference for any disclosure pertinent to the practice of this invention.

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Claims

We Claim:

5 1. A process for preparing cellulose esters having a total DS/AGU of 0.1 to 3.0, said process consisting of contacting the following:

10 (i) a cellulose material,

 (ii) a solubilizing amount of a solvent system comprising either a carboxamide diluent or a urea-based diluent,

15 wherein the carboxamide portion of said carboxamide diluent comprises the structure: $R^4R^5NCOCR^6R^7R^8$, wherein R^4 , R^5 , R^6 , R^7 , and R^8 are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms, and

20 wherein said urea portion of said urea-based diluent comprises the structure: $R^9R^{10}NCONR^{11}R^{12}$, wherein R^9 , R^{10} , R^{11} , and R^{12} are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms,

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(iii) an acylating reagent selected from the group consisting of
(a) an acid chloride, and optionally, an acid acceptor,
5 (b) a carboxylic acid anhydride,
(c) diketene, ketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, and an ester of acetoacetic acid,
(d) an ester of a carboxylic acid,
10 and combinations one or more of (a)-(d),

and

(iv) an insoluble sulfonic acid resin catalyst;
15 wherein said components (i) and (ii) are contacted first and components (iii) and (iv) are contacted with the product of said contacting of components (i) and (ii), in any order.

20 2. A process for preparing cellulose esters having a total DS/AGU of 0.1 to 3.0, said process consisting of contacting the following:

(i) a cellulose material,
25 (ii) a solubilizing amount of a solvent system comprising a carboxamide diluent,
wherein the carboxamide of said carboxamide diluent has the structure: $R^4R^5NCOCR^6R^7R^8$, wherein R^4 , R^5 , R^6 , R^7 , and R^8 are independently selected from the group consisting of hydrogen, alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20

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carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms,

5 (iii) an acylating reagent selected from the group consisting of

(a) an acid chloride, and optionally, an acid acceptor,

(b) a carboxylic acid anhydride,

(c) diketene, ketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, an ester of acetoacetic acid,

10 (d) an ester of a carboxylic acid, and combinations of one or more of (a)-(d),

and

15 (iv) an insoluble sulfonic acid resin catalyst;

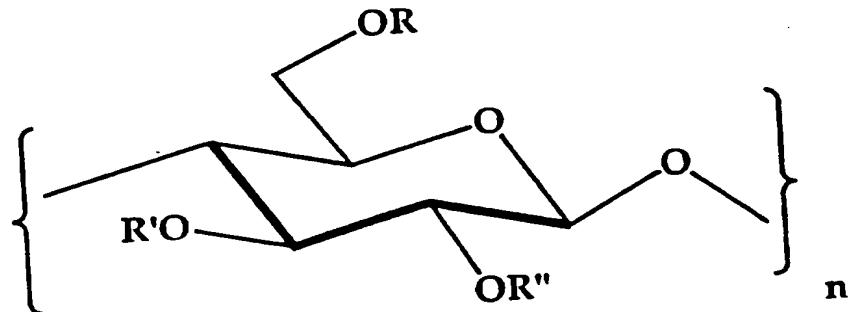
wherein said components (i) and (ii) are contacted first and components (iii) and (iv) are contacted with the product of said contacting of components (i) and (ii), in any order.

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3. The process of Claim 2 wherein said cellulose esters comprise the structure:

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wherein R, R', and R'' are selected separately from the group consisting of: hydrogen, with the proviso that R, R', and R'' are not all hydrogen simultaneously; acetoacetyl; and $R^1C=O$ wherein R¹ is alkyl having from about 1 to about 30 carbons, carboxyalkyl of the structure $(CH_2)_nCO_2H$, where n is from 2 to 6; carboxyalkenyl of the structure, CR²=CR³CO₂H, where R² and R³ are independently selected from the group consisting of hydrogen, 5 methyl, branched alkyl having from about 1 to about 30 carbons, phenyl, and naphthyl; alkenyl having from about 1 to about 30 carbon atoms and from one to three double bonds; and branched alkenyl having from about 1 to about 30 carbon atoms and having 10 from one to three double bonds.

- 15 4. The process of Claim 3 wherein said n of said carboxyalkyl is from 2 to 4.
- 20 5. The process of Claim 3 wherein R, R', and R'' are independently selected from hydrogen, acetyl, propionyl and butyryl.
- 25 6. The process of Claim 2 wherein the amount of cellulose material is about 1.0 percent to about 50 percent, based on the weight of said carboxamide, and the amount of said insoluble sulfonic acid resin catalyst is about 0.1 percent to about 100 percent, based on the weight of said cellulose material.
- 30 7. The process of Claim 2 wherein the amount of cellulose material is about 9 percent to about 28 percent, based on the weight of said carboxamide, and the amount of said insoluble sulfonic acid

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resin catalyst is about 5.0 percent to about 50 percent, based on the weight of said cellulose material.

5 8. The process of Claim 2 wherein the total DS/AGU of the cellulose ester is about 2.0 to about 3.0.

9. The process of Claim 2 wherein the total DS/AGU of the cellulose ester is about 2.4 to about 2.9.

10 10. The process of Claim 2 wherein said carboxamide diluent is selected from the group consisting of 1-methyl-2-pyrrolidinone, N,N-dimethylpropionamide, N,N-diethylacetamide and N,N-dimethylacetamide.

15 11. The process of Claim 1 wherein said carboxamides are selected from the group consisting of succinimides, phthalimides and glutarimides.

20 12. The process of Claim 1 wherein said ester of acetoacetic acid is tert-butyl acetoacetate.

25 13. The process of Claim 1 wherein said carboxylic anhydride is selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, hexanoic anhydride, nonanoic anhydride, lauric anhydride, palmitic anhydride, and stearic anhydride.

30 14. The process of Claim 1 wherein said esters of carboxylic acids are esters formed from the group consisting of the following acids: capric, lauric, palmitic, stearic, oleic, linoleic, linolenic, cyclohexanedicarboxylic, benzoic, substituted benzoic, phthalic, isophthalic and terephthalic.

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15. The process of Claim 1 wherein said acid chloride is selected from the group consisting of acetyl chloride, propionyl chloride, butyryl chloride, hexanoyl chloride, lauroyl chloride, stearoyl chloride.
16. The process of Claim 1 wherein said acid acceptor is selected from the group consisting of pyridine, triethylamine, sodium bicarbonate and sodium acetate.
17. The process of Claim 1 wherein said acid acceptor is pyridine.
- 15 18. The process of Claim 1 wherein said insoluble sulfonic acid resin catalyst is a sulfonated polymer of a mixture comprising a polyvinyl aryl compound and a monovinyl aryl compound.
- 20 19. The process of Claim 1 wherein said insoluble sulfonic acid resin catalyst is a sulfonated copolymer of styrene and divinyl benzene.
- 25 20. The process of Claim 1 wherein said insoluble sulfonic acid resin catalyst is a sulfonated condensation polymer of a phenol and an aldehyde.
- 30 21. The process of Claim 1 wherein said insoluble sulfonic acid resin catalyst is a sulfonated condensation polymer of phenol and formaldehyde.
- 35 22. The process of Claim 1 wherein said cellulose material is selected from the group consisting of hardwood pulp, softwood pulp, cotton linters, bacterial cellulose, and regenerated cellulose.

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23. The process of Claim 1 carried out at a temperature between about 0°C and about 200°C.
- 5 24. The process of Claim 1 carried out at a temperature between about 100°C and about 180°C.
- 10 25. The process of Claim 1 comprising the additional step of separating the insoluble sulfonic acid resin catalyst by filtration for recovery and re-use.
- 15 26. The process of Claim 1 including the additional step of insolubilizing the cellulose ester by addition of an insolubilizing amount of a nonsolvent.
- 20 27. The process of Claim 26 further comprising separating the insolubilized cellulose ester.
28. The process of Claim 26 wherein said nonsolvent is methanol, ethanol, propanol, water, or a mixture thereof.
- 25 29. A product made by the process of Claims 1, 2 or 3.
- 30 30. A process for preparing cellulose esters having a total DS/AGU of 0.1 to 3.0, said process consisting of contacting the following:
 - (i) a cellulose material,
 - (ii) a solubilizing amount of a solvent system comprising a urea-based diluent, wherein said urea-based compound of said urea-based diluent has the structure: $R^9R^{10}NCONR^{11}R^{12}$, wherein R^9 , R^{10} , R^{11} , and R^{12} are independently selected from the group consisting of hydrogen,

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alkyl having from about 1 to about 20 carbon atoms, branched alkyl having from about 1 to about 20 carbon atoms, phenyl, naphthyl, alkenyl having from about 1 to about 20 carbon atoms, and branched alkenyl having from about 1 to about 20 carbon atoms.

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(iii) an acylating reagent selected from the group consisting of

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(a) an acid chloride, and optionally, an acid acceptor.

(b) a carboxylic acid anhydride.

(c) diketene, ketene, 2,2,6-trimethyl-4H-1,3-dioxin-4-one, and an ester of acetoacetic acid,

15

(d) an ester of a carboxylic acid,
and combinations one or more of (a)-(d),

and

(iv) an insoluble sulfonic acid resin catalyst;

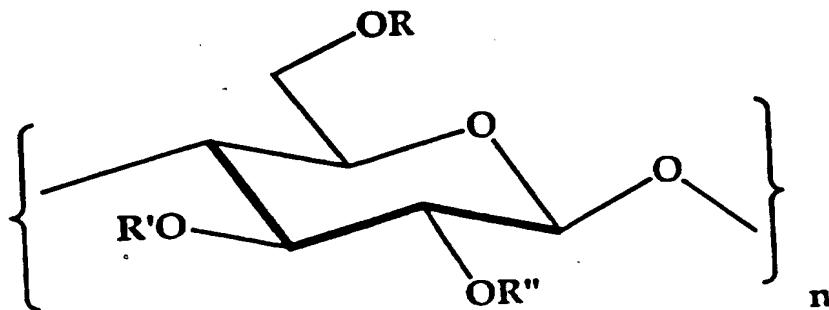
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wherein said components (i) and (ii) are contacted first and components (iii) and (iv) are contacted with the product of said contacting of components (i) and (ii), in any order.

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31. The process of Claim 30 wherein said cellulose esters comprise the structure:

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wherein R, R', and R'' are selected separately from the group consisting of: hydrogen, with the proviso that R, R', and R'' are not all hydrogen simultaneously; acetoacetyl; and $R^1C=O$ wherein R¹ is alkyl having from about 1 to about 30 carbons; carboxyalkyl of the structure $(CH_2)_nCO_2H$, where n is from about 2 to 6; carboxyalkenyl of the structure $CR^2=CR^3CO_2H$, where R² and R³ are independently selected from the group consisting of hydrogen or methyl, branched alkyl having from about 1 to about 30 carbons, phenyl, and naphthyl; alkenyl having from about 1 to about 30 carbon atoms and having from one to three double bonds; and branched alkenyl having from about 1 to about 30 carbon atoms and having from one to three double bonds.

32. The process of Claim 31 wherein said n of said carboxyalkyl is from 2 to 4.

33. The process of Claim 30 wherein one of R⁹ and R¹⁰ and one of R¹¹ and R¹² are connected to form a cyclic urea.

34. The process of Claim 31 wherein R, R', and R'' are independently selected from hydrogen, acetyl, propionyl and butyryl.

35. The process of Claim 31 wherein the amount of cellulose material is about 1.0 percent to about 50 percent, based on the weight of said urea-based compound, and the amount of said insoluble sulfonic acid catalyst is about 0.1 percent to about 100 percent, based on the weight of said cellulose material.

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36. The process of Claim 35 wherein the amount of cellulose material is about 9 percent to about 28 percent, based on the weight of said urea-based compound, and the amount of said insoluble sulfonic acid resin catalyst is about 5.0 percent to about 50 percent, based on the weight of said cellulose material.

5 37. The process of Claim 30 wherein the total DS/AGU of the cellulose ester is about 2.0 to about 3.0.

10 38. The process of Claim 37 wherein the total DS/AGU of the cellulose ester is about 2.4 to about 2.9.

15 39. The process of Claim 31 wherein said urea-based compound is selected from the group consisting of urea and N,N-dimethylimidazolidinone.

20 40. The process of Claim 30 wherein said ester of acetoacetic acid is tert-butyl acetoacetate.

25 41. The process of Claim 30 wherein said carboxylic anhydride is selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, hexanoic anhydride, nonanoic, lauric, palmitic, and stearic.

30 42. The process of Claim 30 wherein said esters of carboxylic acids are formed from the group consisting of the following acids: capric, lauric, palmitic, stearic, oleic, linoleic, linolenic, cyclohexanedicarboxylic, benzoic, substituted benzoic, phthalic, isophthalic and terephthalic.

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43. The process of Claim 30 wherein said acid chloride is selected from the group consisting of acetyl chloride, propionyl chloride, butyryl chloride, hexanoyl chloride, lauroyl chloride, and stearoyl chloride.
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44. The process of Claim 30 wherein said acid acceptor is selected from the group consisting of pyridine, triethylamine, sodium bicarbonate and sodium acetate.
- 10
45. The process of Claim 30 wherein said insoluble sulfonic acid resin catalyst is a sulfonated copolymer of styrene and divinyl benzene.
- 15
46. The process of Claim 30 wherein said insoluble sulfonic acid resin catalyst is a sulfonated condensation polymer of phenol and an aldehyde.
- 20
47. The process of Claim 30 wherein said insoluble sulfonic acid resin catalyst is a sulfonated polymer of a mixture comprising a polyvinyl aryl compound and a monovinyl aryl compound.
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48. The process of Claim 46 wherein said insoluble sulfonic acid resin catalyst is a sulfonated condensation polymer of a phenol and formaldehyde.
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49. The process of Claim 30 wherein said cellulose material is selected from the group consisting of hardwood pulp, softwood pulp, cotton linters, bacterial cellulose, and regenerated cellulose.
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50. The process of Claim 30 carried out at a temperature between about 0°C and about 200°C.

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51. The process of Claim 30 carried out at a temperature between about 100°C and about 180°C.
- 5 52. The process of Claim 30 comprising the additional step of separating the sulfonic acid catalyst by filtration for recovery and re-use.
- 10 53. The process of Claim 30 wherein said acid acceptor is pyridine.
- 15 54. The process of Claim 30 including the additional step of insolubilizing the cellulose ester by addition of an insolubilizing amount of a nonsolvent.
- 20 55. The process of Claim 54 further comprising separating the insolubilized cellulose ester.
56. The process of Claim 54 wherein said nonsolvent is methanol, ethanol, propanol, water, or a mixture thereof.
57. A product made by the process of Claims 30 or 31.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16563

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08B3/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 7649 Derwent Publications Ltd., London, GB; AN 91271X XP002003437 & JP,A,51 119 088 (ASAHI DOW KK) , 20 October 1976 see abstract & CHEMICAL ABSTRACTS, vol. 86, no. 8, 21 February 1977 Columbus, Ohio, US; abstract no. 44988h, page 71; see abstract ---	29,57
Y	---	1-28, 30-56
Y	US,A,2 992 214 (JOHN W. MENCH ET AL.) 11 July 1961 see column 1, line 39 - line 59 ---	1-28, 30-56
		-/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
<p>* Special categories of cited documents :</p> <p>'A' document defining the general state of the art which is not considered to be of particular relevance</p> <p>'E' earlier document but published on or after the international filing date</p> <p>'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>'O' document referring to an oral disclosure, use, exhibition or other means</p> <p>'P' document published prior to the international filing date but later than the priority date claimed</p> <p>'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>'&' document member of the same patent family</p>		
Date of the actual completion of the international search 21 May 1996		Date of mailing of the international search report 05.06.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer Lensen, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16563

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,2 585 516 (J.C.THOMAS) 12 February 1952 see table II see column 1, line 30 - line 45 ---	1-28, 30-56
A	US,A,4 329 446 (WININGER B.S.) 11 May 1982 ---	
A	US,A,2 705 710 (R.C.BLUME) 5 April 1955 cited in the application ---	
A	US,A,2 861 069 (G.P. TOUEY ET AL.) 18 November 1958 cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/16563

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-2992214	11-07-61	NONE	
US-A-2585516	12-02-52	NONE	
US-A-4329446	11-05-82	NONE	
US-A-2705710	05-04-55	NONE	
US-A-2861069	18-11-58	NONE	

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